OFFICE OF NAVAL RESEARCH

Grant N00014-93-1-0351

R & T Code 4J33020- - -09

Technical Report No. 4

The Oxidation of Cysteine, Cysteinesulfinic Acid and Cysteic Acid on a Polycrystalline Gold Electrode

by

W. Ronald Fawcett, Milan Fedurco, Zuzana Kovacova and Zofia Borkowska

Prepared for Publication

in

Journal of Electroanalytical Chemistry

Department of Chemistry
University of California
Davis, CA 95616

April 15, 1993

REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	April 15, 1993	Technical

4. TITLE AND SUBTITLE

The Oxidation of Cysteine, Cysteinesulfinic Acid and Cysteic Acid on a Polycrystalline Gold Electrode

5. FUNDING NUMBERS

N00014-93-1-0351

6. AUTHOR(S)

W. Ronald Fawcett, Milan Fedruco, Zuzana Kovacova and Zofia Borkowska

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Department of Chemistry
University of California
Davis, CA 95616

8. PERFORMING ORGANIZATION REPORT NUMBER

No. 4

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
800 N. Quincy
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Prepared for publication in Journal of Electroanalytical Chemistry

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The mechanism of cysteine, cysteinesulfinic acid and cysteic acid electrooxidation in perchloric acid solutions has been studied using cyclic voltammetry. All compounds investigated have been found to be chemisorbed on a polycrystalline gold electrode and oxidized with four, two or one electron, respectively. The water molecule co-adsorbed with cysteine participates in the latter's one-electron oxidation with a lower energy requirement whereas at the completely covered electrode surface, bulk water is involved in multiple electron transfer reactions. A strong inhibiting effect of chloride anions on cysteine oxidation has been observed at the partially covered electrode surface. The effect of adsorbate surface coverage on the reaction mechanism in anodically catalyzed reactions involving oxygen transfer is discussed.

14. SUBJECT TERMS	15. NUMBER OF PAGES
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclassified	unclassified	unclassified	unclassified

The Oxidation of Cysteine, Cysteinesulfinic Acid and Cysteic Acid on a Polycrystalline Gold Electrode.

W. Ronald Fawcett, Milan Fedurco, Zuzana Kovacova and Zofia Borkowska

Department of Chemistry
University of California
Davis, CA 95616

ABSTRACT

The mechanism of cysteine, cysteinesulfinic acid and cysteic acid electrooxidation in perchloric acid solutions has been studied using cyclic voltammetry. All compounds investigated have been found to be chemisorbed on a polycrystalline gold electrode and oxidized with four, two or one electron, respectively. The water molecule co-adsorbed with cysteine participates in the latter's one-electron oxidation with a lower energy requirement whereas at the completely covered electrode surface, bulk water is involved in multiple electron transfer reactions. A strong inhibiting effect of chloride anions on cysteine oxidation has been observed at the partially covered electrode surface. The effect of adsorbate surface coverage on the reaction mechanism in anodically catalyzed reactions involving oxygen transfer is discussed.

INTRODUCTION

The adsorption of organic compounds and their redox reactions from the adsorbed state have been extensively studied during the last few decades on a great variety of electrodes. The control of short range structuring forces at the electrode solution interface by means of chemical modification [1,2] has led to a better understanding of

phenomena such as electron transfer over large distances, photocorrosion, corrosion, and electrocatalysis.

Electrocatalysis is one of the most complex topics in electrochemistry since adsorption of the reactant usually proceeds multiple electron transfer. Its progress is often determined using modern techniques for in-situ interface characterization [3,4]. A large number of organic molecules such as aldehydes, alcohols, and inorganic ligands such as SO_3^{2-}, $S_2O_3^{2-}$ and NO_2^- undergo oxidation from the adsorbed state in the potential region of gold preoxidation and/or gold oxide formation [5]. In these cases, cyclic voltammetry can give very useful information about the state of the electrode surface and the electrode process in a single experiment.

An important issue in understanding the mechanism of "surface controlled" anodic reactions involving oxygen transfer is *whether* and *how* the species co-adsorbed with the reactant, for example water molecules, participate in the oxidation process. A general scheme has been proposed [5] for both alkaline and acidic media involving a submonolayer of adsorbed hydroxyl radicals at the electrode surface in the electrocatalytical oxidation mechanism :

$$OH^- \rightleftharpoons {}^{\cdot}OH + e^- \qquad (1)$$

The hydroxyl radical is suggested to be involved in the chemical steps following the extraction of electrons from the adsorbed reactant. The existence and the role of hydroxyl radicals in these anodic reactions, especially in

acidic solutions where the surface concentration of OH^- anions in the double layer region is expected to be low, is not very clear. A more complex species, namely, $Au_2(OH)_9^{3-}$ has been suggested to exist in the preoxidation region of gold and to be involved in anodic electrocatalytic reactions [6,7].

Thiols and disulfides are known to be irreversibly adsorbed (chemisorbed) on metal electrodes such as Au, Pt, and Hg. Analytical techniques using mercury or mercury amalgam electrodes involve reductive desorption of the corresponding mercaptides from mercury [8]. On the other hand, organosulfur compounds undergo oxidative desorption at positively charged electrodes. This phenomenon is widely used in voltammetric and amperometric quantitative detection on solid electrodes [9]. During oxidative desorption from solid electrodes sulfonated products from the chemisorbed sulfur compounds are formed. Multielectron transfer then gives a larger analytical response than in the case of reductive desorption. One can expect the dependence of current on sulfur compound concentration in this type of reaction to be determined by the adsorption of reactants including water molecules which then take part in the chemical reactions following electron transfer. Therefore, it is important to study these oxidation processes at a partially covered electrode surface.

In the present work we have chosen to study a water soluble amino acid cysteine (RSH). Cysteinesulfinic acid

(RSO_2H) and cysteic acid (RSO_3H) are expected to be among the products of oxidation of cysteine on a gold electrode. Electrode processes of cystine and cysteine on platinum and gold electrodes in 1.0 M H_2SO_4 solutions were reported earlier [10-12]. However, neither the number of electrons nor the product in the electrooxidation reactions on a gold electrode were established. The technique used here to determine a possible mechanism for anodic surface reactions in acidic solutions is cyclic voltammetry. The key role of water in these oxidation reactions and the way it participates in the overall process is discussed in this paper.

EXPERIMENTAL

Reagents

Solutions of supporting electrolyte were prepared by dilution of redistilled 99.999% $HClO_4$ (Aldrich) in water. DL-cysteine, L-cysteinesulfinic acid monohydrate (99 %) and L-cysteic acid monohydrate (98 %) were purchased from Sigma Chemical Co. and used as received. Fresh solutions were prepared a few minutes before starting the experiment in ultrapure water. Potassium chloride (99+ % pure), (A.C.S. certified, Aldrich) was twice recrystallized from water and dried at 150 ^{o}C under reduced pressure for 24 hours.

Apparatus and procedures

Instrumentation

Cyclic voltammetric experiments were performed using the EG&G/PAR 273 potentiostat or alternatively with a system made up of a EG&G/PAR 175 Universal Programmer, EG&G/PAR Electrometer Probe (Model 178) and a EG&G/PAR 176 Current Follower. The output current and voltage were recorded on an X-Y Recorder BD 91 (Kipp & Zonen).

Water and glass purification

All water used in the experiments was prepared in a Barnstead water purification system, and had a resistivity in the range 17.8 - 18.0 MΩ cm. All parts of the electrochemical cell (pyrex glass), the glassware used for the preparation of solutions and electrode annealing were washed with Alconox detergent (Aldrich), extensively washed with distilled water and boiled in HNO_3 (1:1) for at least one hour; they were kept overnight in the same solution in order to oxidize organic impurities. The glass was again boiled in the acid solution for a short period of time. Glass parts were taken out of the acid with a long glass tube preventing possible contamination with gloves, and rinsed in a stream of distilled water. Before starting the experiment all glass flasks not being immediately used were

kept filled with ultrapure water and closed with a glass stopper.

The gold electrode

The working electrode was a polycrystalline gold rod (99.995 % pure) prepared by fusion in a graphite mold (diameter 2.54 mm) at 1200 ^{o}C under vacuum. The rod was then washed with aqua regia to remove the top layer of gold with collected impurities. The gold electrode surface was prepared in a following way: the gold rod was placed in a teflon holder and polished with fine carborundum paper (Buehler), diamond paste (Buehler, 3 μm), and then alumina (Buehler, 1 μm, 0.3 μm and 0.05 μm, successively) on a polishing wheel. Only minor scratches appeared under an optical microscope (magnification 100x). Electrical contact was made via a gold wire at one end of the rod. The working electrode was then electropolished for 10 minutes by potentiodynamic cycling in 0.01 M $HClO_4$ in the potential range from -0.5 V to +1.3 V against a calomel electrode containing 0.05 M KCl. The electrode surface was flame annealed in a natural gas-air flame (pretreatment in a hydrogen-oxygen flame gave the same CV response), cooled in ultrapure water for about 30 seconds, and protected with a drop of water before being transferred to the cell. Contact with the solution was made by the hanging electrolyte method at an applied potential of -0.5 V only after ten minutes of

solution purging with pure nitrogen (99.997 %). During the time of oxygen removal, the working electrode was kept above the solution in order to prevent the adsorption of cysteine at the electrode surface. The working electrode was annealed before any new addition of a sulphur compound to the polarographic solution. The surface area of the working electrode in contact with the solution was 0.057 cm^2. The apparent geometric area of the cylinder was determined using dial calipers to measure the diameter of the gold rod after completion of the electrochemical experiments. A roughness factor n = 1.12 was estimated from the charge needed to form a monolayer of gold oxide by integrating the current-potential profile to the potential of the Burshtein minimum [13] and then comparing this result with the geometric area of the gold electrode.

The working electrode was mounted in a glass tube between two Teflon holders which allowed the vertical position of the electrode to be varied continuously. The electrode system was clamped to the body of the cell via a ball-joint which allowed variation in the angle with which the end of the gold cylinder came into contact with the solution.

The cell and other electrodes

The cell was of conventional design and incorporated the gold working electrode, a gold counter-electrode and a

calomel reference electrode using 0.05 M KCl (0.097^{+}0.001 V positive of the saturated calomel electrode). The counter electrode was a gold wire spiral of relatively large surface area. It was submitted to the same chemical treatment as the working electrode and flame annealed before being placed in the cell. The reference electrode was connected to the main body of the cell through a Luggin capillary. All experiments were performed at room temperature 23 $^{+}$ 1 ^{o}C.

The transfer experiment

Two electrochemical cells as described in the previous section were used in the experiments involving oxidative desorption of sulfur containing compounds from the electrode surface. The cleanliness of the gold electrode/solution interface was checked in both cells by cycling the potential to the region of gold oxide formation. Any further experiments were performed only when a steady state was reached after the first sweep in the potential range studied (from -0.5 V to + 1.3 V).

The adsorbates investigated in the transfer experiment were chemisorbed on the gold electrode surface under potential control. Then the electrode was removed from the solution with a drop of electrolyte and immediately placed in a beaker containing ultrapure water. The electrode was constantly kept in the beaker and extensively washed in a stream of water from the Barnstead water purification system

for at least one minute. Then the electrode was transferred to the test solution with a drop of ultrapure water, and oxygen removed from the cell by passing nitrogen for 10 minutes. The adsorbate was desorbed from the electrode surface in an anodic potential sweep. The same "transfer experiment" with a bare electrode surface was conducted prior to the adsorption of the sulfur compound to ensure that the electrode surface was not contaminated by transfer to another cell.

RESULTS AND DISCUSSION

Electrooxidation of cysteine

The oxidation of cysteine was studied in 0.01 M HClO4 on a polycrystalline gold electrode using cyclic voltammetry. Figure 1a shows a cyclic voltammogram recorded in the potential range from -0.5 V to + 1.3 V after flame annealing without any previous cycling to the gold oxidation region. With the first cycle in this experiment steady state is achieved, no changes being observed with further cycling. The potential region of gold oxidation can be clearly distinguished from the double layer region with the potential of zero charge (pzc) at a scan rate of 500 mV s^{-1} (Fig. 1b). The cyclic voltammogram and pzc in this medium are in good agreement with results published previously by Clavilier and co-workers [14].

The oxidation of 1.2 μM RSH on the gold electrode in a dilute solution of perchloric acid is shown in Figure 2. Current peak **B**, which has been assigned to deposition of hydroxyl ions on polycrystalline gold accompanied by desorption of perchlorate anions [15], is partially suppressed in the presence of adsorbed cysteine. Anodic peak **A** appears at a potential about 50 mV more negative than the onset of gold hydroxide formation. A significant increase in the anodic current is observed in the potential region of surface gold oxide formation at + 0.95 V (peak **C**). The following experiment was made in order to elucidate the nature of peaks **A** and **C**. A positively going potential scan was reversed at +0.75 V. It clearly gave no cathodic current but peak **B** after the reversal of sweep at +0.85 V still has its cathodic counterpart, designated, peak $\mathbf{B_1}$. From this observation we conclude that peak **A** corresponds to the irreversible oxidation of cysteine and not to gold oxidation.

If the positively going scan is stopped at +0.5 V and the working electrode with adsorbed cysteine is transferred to another cell containing 0.01 M $HClO_4$, after an extensive wash with ultrapure water, the cyclic voltammogram recorded is identical to that shown in Fig. 2 (solid curve). The curve obtained on the second potential sweep is the same as a bare electrode surface (dotted curve). These experiments confirm that cysteine is chemisorbed on the polycrystalline gold electrode and that all of the cysteine previously

adsorbed in the double layer region can be quantitatively transferred from one cell to another and oxidatively desorbed from the electrode surface.

In the next experiment, with the same concentration of cysteine and experimental conditions described above, we repeated the transfer of a cysteine modified gold electrode to another cell, in order to determine if the final product of cysteine oxidation has already been formed in peak **A**. The potential was held at +0.75 V (see Fig. 2), the solution stirred for five minutes, and then potential cycling continued to + 1.3 V. No significant change in the charge passed in anodic peak **C** was observed indicating that there are two steps in the oxidation of chemisorbed cysteine. Electron transfer takes place at a potential of +0.71 V (peak **A**) and a reaction intermediate is formed which remains adsorbed on the electrode surface. The oxidation product is desorbed from the electrode surface in peak **C** only after a multiple electron transfer reaction.

A "dipping procedure" is often used for chemical modification of solid metal electrodes with organosulfur compounds [2]. The time needed to obtain full surface coverage of thiols or disulfides may vary on Au or Pt from a few seconds to 24 hours [16]. The deposition time is expected to depend on electrode material, the structure of adsorbate, its bulk concentration, the solvent used and whether the solution is stirred. Cysteine is very reactive

towards gold and therefore special procedures have to be used in the cyclic voltammetric experiment in order to control surface coverage.

It is evident from Fig. 3a that when the bulk concentration of cysteine is low there is a visible difference in the amount of oxidation product after completion the forward half of the first cycle (dotted curve), with respect to that found after two cycles (solid curve). The total anodic charge does not change after further cycling of the potential (from -0.5V to + 1.3 V) since the total time spent in the double layer region is always about two minutes at a scan rate of 20 mV s^{-1}. Stirring of solution has the largest effect on the amount of product oxidatively desorbed from the electrode surface in the case of small concentrations of RSH in the bulk of the solution (see Fig. 3b). An arrow in Figures 4a-c indicates a decrease or increase in anodic current with a new addition of organosulfur compound. As the bulk concentration of RSH increases to $2x10^{-5}$ M (Fig 4a), stirring becomes less and less important. The first and any other cycle is identical for bulk RSH concentrations greater than $2x10^{-5}$ M at a scan rate 20 mV s^{-1}. Under these conditions full surface coverage is reached in the order of a few seconds. Further increase of bulk RSH concentration results in a large oxidation current superimposed on the anodic current from the adsorbed state (see Fig. 4b and Fig. 5, curve a). It disappears in the transfer experiment, indicating diffusion-

controlled oxidation of cysteine molecules from the bulk of the solution.

The total charge for the oxidation of cysteine from the adsorbed state Q_{RSH}^{ox} can be determined in two ways. Firstly, one can find the capacity-potential curve corresponding to full cysteine surface coverage. The monolayer is then oxidatively desorbed from the electrode surface in the absence of RSH in the solution. Secondly, the cysteine can be chemisorbed on Au at constant potential in the double layer region from its solutions with a bulk concentration greater than 2×10^{-5} M.

It follows from our experiments that

$$Q_{Au}^{ox} = Q_{Au}^{red} \quad (2)$$

$$Q_{RSH}^{ox} = Q_t^{ox} - Q_{Au}^{ox} \quad (3)$$

$$Q_{RSH}^{ox} = (Q_A + Q_C) - Q_{Au}^{ox} \quad (4)$$

$$Q_A = Q_B \quad (5)$$

$$Q_C = 3\, Q_A \quad (6)$$

where Q_{Au}^{ox} is the charge needed to form a monolayer of gold oxide on the bare electrode surface, Q_{Au}^{red}, the charge needed for gold oxide reduction, Q_t^{ox}, the total anodic charge passed in the oxidation region of gold negative of + 1.3 V in the presence of cysteine, Q_A, the charge passed in the anodic peak A in the presence of cysteine (shaded area in Fig. 2), Q_B, the difference in the charge passed in the anodic peak B for gold hydroxide formation on the bare

electrode surface and on that partially blocked by cysteine (shaded area in Fig. 2), and Q_C, the difference in the charge passed in anodic peak **C** in the presence and in the absence of cysteine (shaded area in Fig. 2).

The potentiodynamic sweep experiments revealed that the oxidation of cysteine at full surface coverage, after electrode transfer to a solution of 0.01 M $HClO_4$, and potential scan reversal at +0.85 V, is a completely irreversible process. No cathodic current corresponding to gold hydroxide reduction at a fully covered electrode surface is observed.

Effect of chloride anions on cysteine oxidation

The effect of chloride anions on the oxidation of gold is shown in Fig. 6a. The deposition of hydroxyl ions on gold (peak **B**) is inhibited in the presence of 1.0 mM KCl and the gold oxidized at more positive potentials. Jiang et al. [17] studied the adsorption of chloride anions on a polycrystalline gold electrode using a piezoelectric technique combined with a.c. admittance measurements. They concluded that chloride anion is specifically adsorbed with a potential dependent partial charge transfer to the metal. For a surface coverage of cysteine smaller than 60%, a strong inhibitive effect of Cl^- on cysteine oxidation at +0.71 V as well as on the deposition of the OH^- species (suppression of the peak **B**) is observed (Fig. 6b). A small

peak corresponding to cysteine oxidation in the presence of chloride, denoted as A_{KCl}, can still be observed. It is probable that all the water molecules cannot be removed quantitatively from the electrode surface for this surface excess of chloride anions. Further cysteine surface compound oxidation is pushed towards more positive potentials and coincides with the large anodic current caused by electrodissolution of gold and formation of different Au-Cl species as discussed by Herrera Gallego et al. [18]. It is interesting that the peak A_{KCl} peak appears in the presence of 1.0 mM KCl at slightly more negative potentials. This phenomenon and the small capacitative peaks D and D_1 appearing at +0.69 V (Fig. 6c) are not completely understood. They might be connected with gold surface reconstruction or rearangement of adsorbate molecules. Further experiments performed by the a.c. admittance technique have shown that there is no effect of chloride anions on the capacity-potential curve for full surface coverage by cysteine ($2x10^{-5}$ M RSH and $1x10^{-3}$ M KCl). Cysteine replaces the chloride anion quantitatively from the electrode surface. The effect of Cl^- on cysteine electroxidation at full surface coverage is also negligible. The integrated area Q_{RSH} obtained in the presence of 1.0 mM KCl is the same as that in the absence of chlorides.

Oxidation of RSO_2H

To understand better the mechanism of cysteine oxidation on a gold electrode from the adsorbed state we studied the oxidation of cysteinesulfinic acid in the same way as described above. It is surprising that both compounds RSH and RSO_2H are chemisorbed at the electrode surface and that their voltammetric behaviour in the potential region of gold oxidation is rather similar. The charge passed in the integrated area Q_P is almost identical (Fig. 7a) with the charge Q_A for the cysteine oxidation with the same bulk concentration of compounds (recorded under identical experimental conditions). A difference is evident in the potential region of further adsorbed intermediate oxidation at + 0.95 V. The ratio of Q_P to Q_R is 1 to 1 in the case of cysteinesulfinic acid. The oxidation of RSO_2H from the bulk is superimposed on the oxidation from the adsorbed state just as in the case of cysteine (see Fig. 5, curve b and Fig. 7b).

Oxidation of RSO_3H

It is known [19] that, even in the case of sulfonic acid, where the sulfur atom is in its maximum possible oxidation state, further oxidization with cleavage of the C-S bond is possible. There is again a visible prewave at a potential of +0.73 V for small surface coverages of RSO_3H (Fig. 8). No faradaic current contributing to bulk RSO_3H oxidation is

observed in the concentration range from $1x10^{-5}$ M to $1x10^{-2}$ M RSO_3H (see Fig. 5, curve c). The total anodic charge Q (negative of +1.3 V) does not change with concentration of RSO_3H but the onset potential for the surface compound oxidation is very much shifted towards more positive potentials. This can be explained by multilayer formation which can eventually decrease the surface concentration of water molecules. The accumulation of $1x10^{-4}$ M RSO_3H on polycrystalline gold or Au(111) electrodes at +0.5 V for 5 minutes resulted in a film which could be transferred to another cell and oxidatively desorbed from the electrode surface in spite of an extensive wash with distilled water. We conclude that cysteic acid can be oxidized on a gold electrode in the potential range investigated only after prior adsorption on the electrode surface.

Mechanism of RSH, RSO_2H and RSO_3H oxidation

Cysteine is known to be oxidized in a homogeneous chemical reaction with periodate and other strong oxidizing agents [20]:

$$RSH + IO_3^- \rightleftharpoons RSO_3H + I^- \qquad (7)$$

The sulfur atom in this reaction changes valence from (2-) to (4+) so that six electrons are involved in the overall reaction. The nature of the product of cysteine electrooxidation in the chemisorbed state is an open

question. When the charge for the oxidation of all three compounds from the adsorbed state is plotted against the logarithm of bulk concentration (Fig. 5) one sees that the charge Q tends to reach a plateau (broken line) which represents full surface coverage (determined as the average from eight transfer experiments). All the points corresponding to less than monolayer coverage represent non-equilibrium data.

An interesting finding appears when the prewaves for RSH (Fig. 4a) and for RSO_2H (Fig. 7a) are compared. The ratio of charges Q_A to Q_C and Q_P to Q_R for both compounds is 1 : 3 and 1 : 1, respectively. This might mean that both chemisorbed compounds undergo a one-electron oxidation at about +0.7 V since their solubility in water and diffusion coefficients are similar. In the second peak at +0.95 V both compounds are further oxidized with 3 electrons and 1 electron, respectively and desorbed from the electrode surface (compare Fig. 4a and Fig. 7a). We would like to stress that all three compounds have no significant effect on charge passed in the cathodic peak C_1 (see Fig. 4, 7 and 8) at any surface coverage of adsorbate studied in this work. This means that the amount of gold oxide formed at the electrode surface after the desorption of the product of oxidation of any of the compounds considered here is the same. Cyclic voltammetry can serve as an important tool to control surface coverage of water soluble organosulfur compounds in acidic media. The adsorption of these

compounds starts in the double layer region immediately after the completion of gold oxide reduction (negatively-going potential sweep) and ends up with their oxidation and following desorption in the potential region of gold oxide formation (positive polarisation of the Au electrode).

A possible reaction mechanism for the three compounds investigated can be written in the following equations:

I. Cysteine electrooxidation on gold

$$AuSR + 2\ H_2O \longrightarrow Au^+ + RSO_2H + 4e + 3\ H^+ \quad (8)$$

$$Au^+ + H_2O \rightleftharpoons AuOH + H^+ \quad (9)$$

$$Au\text{-}OH \rightleftharpoons AuO + 1e + H^+ \quad (10)$$

$$RS\text{-}Au + 3\ H_2O \longrightarrow RSO_2H + AuO + 5e + 5\ H^+ \quad (11)$$

II. Cysteinesulfinic acid electrooxidation on gold

$$AuSO(OH)R + H_2O \longrightarrow Au^+ + RSO_3H + 2e + 2\ H^+ \quad (12)$$

$$Au^+ + H_2O \rightleftharpoons AuOH + H^+ \quad (13)$$

$$AuOH \rightleftharpoons AuO + H^+ + 1e \quad (14)$$

$$RSO_2H\text{-}Au + 2\ H_2O \longrightarrow RSO_3H + AuO + 3e + 4H^+ \quad (15)$$

III. Cysteic acid electrooxidation on gold

$$RSO_3H \rightleftharpoons RSO_3^- + H^+ \quad (16)$$

$$AuO_3SR + H_2O \longrightarrow HSO_3^- + RH + OH^- + 1e \quad (17)$$

$$OH^- + H^+ \rightleftharpoons H_2O \quad (18)$$

Water involvement in anodic oxidation reactions

It appears to us that cysteine might be a suitable model compound for a number of reactants undergoing surface controlled anodic reactions in acidic solutions. The chemisorption of cysteine from 0.01 M $HClO_4$ takes place at potentials negative of -0.6 V (hydrogen evolution region in Fig. 1b) and results in a one-electron oxidation of compound:

$$Au + RSH \rightleftharpoons Au\text{-}SR + H^+ + e^- \qquad (19)$$

At a surface coverage smaller than about 60% of a monolayer we observed that water co-adsorbed with cysteine molecules at the electrode surface participates in another one-electron oxidation reaction at about +0.7 V against the calomel electrode. Since the water molecules interact strongly with the positively charged gold electrode surface, the O-H bond is labilized upon adsorption of water at highly positive charge densities. After the extraction of one electron from the sulfur atom at E_p = +0.71 V, adsorbed water chemically reacts with the cation radical of gold mercaptide and forms its hydroxylated product still bound to the electrode surface in an irreversible chemical reaction. We have found that, at full surface coverage of cysteine, water molecules are not co-adsorbed with cysteine so that bulk water instead participates in the oxidation of the tightly packed chemisorbed compound. This process is

energetically less favourable and therefore takes place at a more positive potential, that is, approximately +0.85 V (see Fig. 4b, peak A_1). At E_p = +0.95 V the hydroxylated surface compound is further oxidized to RSO_2H and desorbed from the electrode surface. Both the electrooxidation of cysteine and gold oxide formation are pH dependent processes. Therefore it would be interesting to compare the oxidation of cysteine in both acidic and alkaline media. Unfortunately, cysteine decomposes in alkaline solutions of pH > 6 [21].

Since most of the electrocatalytic anodic reactions involving oxygen transfer have been studied in alkaline media we would like to stress that the extent of gold hydroxide formation on low-index gold single crystal electrodes such as Au(111), Au(100) and Au(110) [15,22,23] differs significantly from that on polycrystalline gold, and should not be used as a proof of gold hydroxide existence in the double layer region on a polycrystalline electrode. On the other hand, the surface structure of polycrystalline gold and that of highly stepped gold surfaces are similar. In addition, Hamelin et al. [24] found that the current - voltage features in cyclic voltammetric experiments for gold oxide formation/reduction on monocrystalline surfaces in alkaline (0.11 M NaOH) and acidic media (0.01 M $HClO_4$) are closely similar. Hydroxyl ions were found to be specifically adsorbed on Au(210) but no faradaic processes (OH^- oxidation) in the double layer region were observed .

The fact that the charge connected with the gold oxide formation in both media is identical and that the deposition of hydroxyl ions takes place in the sharp current peak (as in 0.01 M $HClO_4$) is evidence that the surface concentration of hydroxyl radicals (reaction (1)) in the double layer region is insignificant and comparable with what occurs in acidic media. Since most electrocatalytic anodic reactions involving oxygen transfer take place via prior reactant adsorption, the water molecules or OH^- anions (depending on the pH of the solution) can be removed in a number of cases from the electrode surface with an increase in the adsorbate surface coverage. This is determined mainly by the Gibbs energy of adsorption (ΔG_{ads}) of the reactant and the energy of the chemical bond between the adsorbate and the metal. This should be considered before making any conclusions about the presence of hydroxyl radicals at the electrode surface. *The fact that the oxidation reaction takes place from the adsorbed state in the potential region of gold hydroxide/oxide formation does not necessarily mean that a monolayer of Au-OH species is present at the electrode surface.* Additional knowledge about the surface coverage of adsorbates is required from independent measurements.

In order to determine a possible reaction mechanism for anodic oxygen transfer involving reactions from cyclic voltammetric data, the charge corresponding to the surface-controlled oxidation of reactant should be always separated from that controlled by diffusion of the electroactive

species from the bulk of the solution. This can be easily done in "transfer experiments". The oxidation of cysteine on gold electrodes from the bulk of the solution results probably in different reaction products than its oxidation from the adsorbed state [11]. However, a discussion of these phenomena is beyond the scope of the present paper.

CONCLUSIONS

The work presented shows that all compounds studied, cysteine, cysteinesulfinic acid and cysteic acid are adsorbed on polycrystalline gold electrode and undergo 4e, 2e and 1e oxidation from the adsorbed state, respectively. Gold hydroxide/oxide formation has been shown to be inhibited in the presence of sulfur containing adsorbates. The way in which water molecules participate in anodic surface reactions is controlled by the surface coverage of chemisorbed compounds. We anticipate that different parameters are important in the anodic electrocatalytic reactions involving oxygen transfer, for example, crystallographic orientation of the electrode material, the structure of adsorbate and its size, packing density of molecules on the electrode surface, molecular interactions, and multilayer formation. This will be discussed in a series of papers reporting experiments recently performed in this laboratory.

ACKNOWLEDGEMENT

We gratefully acknowledge the support of the Office of Naval Research, Washington.

REFERENCES

1. A.G. Somorjai, Chemistry in Two Dimensions: Surfaces, Cornell University Press, Ithaca-London (1981) Chap. 2.
2. R.W. Murray (Ed.), Molecular design of electrode surfaces, John Willey & Sons, Inc., New York (1992).
3. C. Cutierrez and C. Melendres (Eds.), Spectroscopic and Diffraction Techniques in Interfacial Electrochemistry, NATO ASI Series, Kluwer Academic Publishers, Dordrecht (1990).
4. D.H. Abruna (Ed.), Electrochemical Interfaces: Modern techniques for in-situ interface characterization, VCH Publishers, Inc., New York (1991).
5. J.E. Vitt, L.A. Larrew and D.C. Johnson, Electroanalysis, 2 (1990) 21, and references therein.
6. D.L. Burke and V.J. Cunnane, J. Electroanal. Chem., 210 (1986) 69.
7. L.D. Burke and J.F. O'Sullivan, Electrochim. Acta, 37 (1992) 2087, and references therein.
8. W.F. Smyth, Voltammetric Determination of Molecules of Biological Significance, John Wiley & Sons Ltd., Chichester (1992) pp. 54-63.

9. Z.T. Polta and D.C. Johnson, J. Electroanal. Chem., 209 (1968) 159., and references therein.

10. J. Pradac and J. Koryta, J. Electroanal. Chem., 17 (1968) 167

11. J. Koryta and J. Pradac, J. Electroanal. Chem., 17 (1968) 177.

12. J. Koryta and J. Pradac, J. Electroanal. Chem., 17 (1968) 185.

13. R. Woods in Electroanalytical Chemistry, A.J. Bard (Ed.), Marcel Dekker, New York (1976) vol. 9, pp. 119-125.

14. J. Clavilier and N.C. van Huong, J. Electroanal. Chem., 80 (1977) 101.

15. H. Angerstein-Kozlowska, B.E. Conway, A. Hamelin and L. Stoicoviciu, Electrochim. Acta, 31 (1986) 1051.

16. E.Y. Katz and A.A. Solov'ev, J. Electroanal. Chem., 291 (1990) 171.

17. X.C. Jiang, M. Seo, and N. Sato, J. Electrochem. Soc., 137 (1990) 3804.

18. J. Herrera Gallego, C.E. Castellano, A.J. Calandra and A.J. Arvia, J. Electroanal. Chem., 66 (1975) 207.

19. H. Lund and M.M. Baizer (Eds.), Organic electrochemistry. An Introduction and a guide, Third edition, Marcel Dekker, New York (1991) pp. 659-698.

20. M. Friedman, The Chemistry and Biochemistry of the Sulphydryl Group in Amino Acids, Peptides and Proteins,

Pergamon Press, Oxford (1973) p. 64.

21. Ref. 20, Chap. 5

22. A. Hamelin, J. Electroanal. Chem., 255 (1988) 281.

23. A. Hamelin, J. Electroanal. Chem., 329 (1992) 247.

24. A. Hamelin, M.J. Sottomayor, F. Silva, S.-C. Chang and M.J. Weaver, J. Electroanal. Chem., 295 (1990) 291.

Legends for Figures

Figure 1 **a)** Cyclic voltammogram for a polycrystalline gold electrode in 0.01 M $HClO_4$, at a scan rate of 20 mV s^{-1}.

b) The same as a) extended to the potential region of hydrogen evolution at a scan rate of 20 mV s^{-1}. Current-voltage characterictics were also recorded in the double layer region at a scan rate of 500 mV s^{-1}.

Figure 2 Potentiodynamic sweeps for the oxidation of $8x10^{-7}$ M cysteine (solid curve) and gold oxide formation in a solution without cysteine (dotted curve) with 0.01 M $HClO_4$ at a scan rate of 20 mV s^{-1}.

Figure 3 **a)** Effect of the number of potential sweeps on the oxidation of $8x10^{-8}$ M cysteine in the potential region from -0.5 V to + 1.3 V with a fresh electrode (dotted curve) and after completing two potential cycles (solid curve) at 20 mV s^{-1}.

b) As in Fig. 3a., but with stirring of the solution at 60 r.p.m. .

Figure 4 a) Current-voltage response in 0.01 M $HClO_4$ with increasing bulk concentration of cysteine: 0; 0.08; 0.2; 0.4; 0.8; 1.2 μM RSH at a scan rate of 20 mV s^{-1}.

b) As in Fig. 4a, but for 2.0 and 20.0 μM RSH. The dotted curve shows results for a transfer experiment on a gold electrode in which cysteine was allowed to adsorb from a 100.0 μM RSH solution for 60 s at +0.3 V and then transferred to a cell containing 0.01 M $HClO_4$ and cycled once between + 0.3 V and + 1.3 V at the same scan rate.

Figure 5 The total charge for the oxidation of various organosulfur compounds on gold plotted versus the logarithm of bulk concentration: RSH (circles), RSO_2H (triangles) and RSO_3H (squares). Experimental conditions are described in the text.

Figure 6 a) Cyclic voltammetric curves illustrating the inhibitive effect of chloride ions on the deposition of hydroxyl ions on a polycrystalline gold electrode in 0.01 M $HClO_4$. The concentration of KCl is adjacent to each curve. Scan rate:

20 mV s-1.

b) Cyclic voltammogram wit 8x10-7 M RSH in 0.01 M $HClO_4$ (dotted curve), and with the same medium plus 1.0 mM KCl (solid curve).

c) The same as in Fig. 6b but with the current scale enlarged for the potential region from -0.5 V to +0.85 V.

Figure 7

a) Cyclic voltammograms for the oxidation of cysteinesulfinic acid on Au in 0.01 M $HClO_4$ for various bulk concentrations: 0.1; 0.2; 0.4; 0.8 and 1.2 μM RSO_2H. The dotted curve is for a solution with no organosulfur compound.

b) As is Fig. 7a but for 10.0 and 100.0 μM RSO_2H. The dotted curve shows results of a transfer experiment after accumulation from 100 μM RSO_2H at +0.3 V for 5 minutes, transfer to a solution containing 0.01 M $HClO_4$, and scanning from + 0.3 to + 1.3 V. Scan rate: 20 mV/s

Figure 8

Cyclic voltammograms for the oxidation of cysteic acid on Au in 0.01 M $HClO_4$ for various bulk concentrations: 1.0; 10.0; 100.0 and 1000.0 μM RSO_3H. The dotted curve is for a solution with no

organosulfur compound. Scan rate: 20 mV s^{-1}. Cathodic peak C_1 is discussed in in the text.

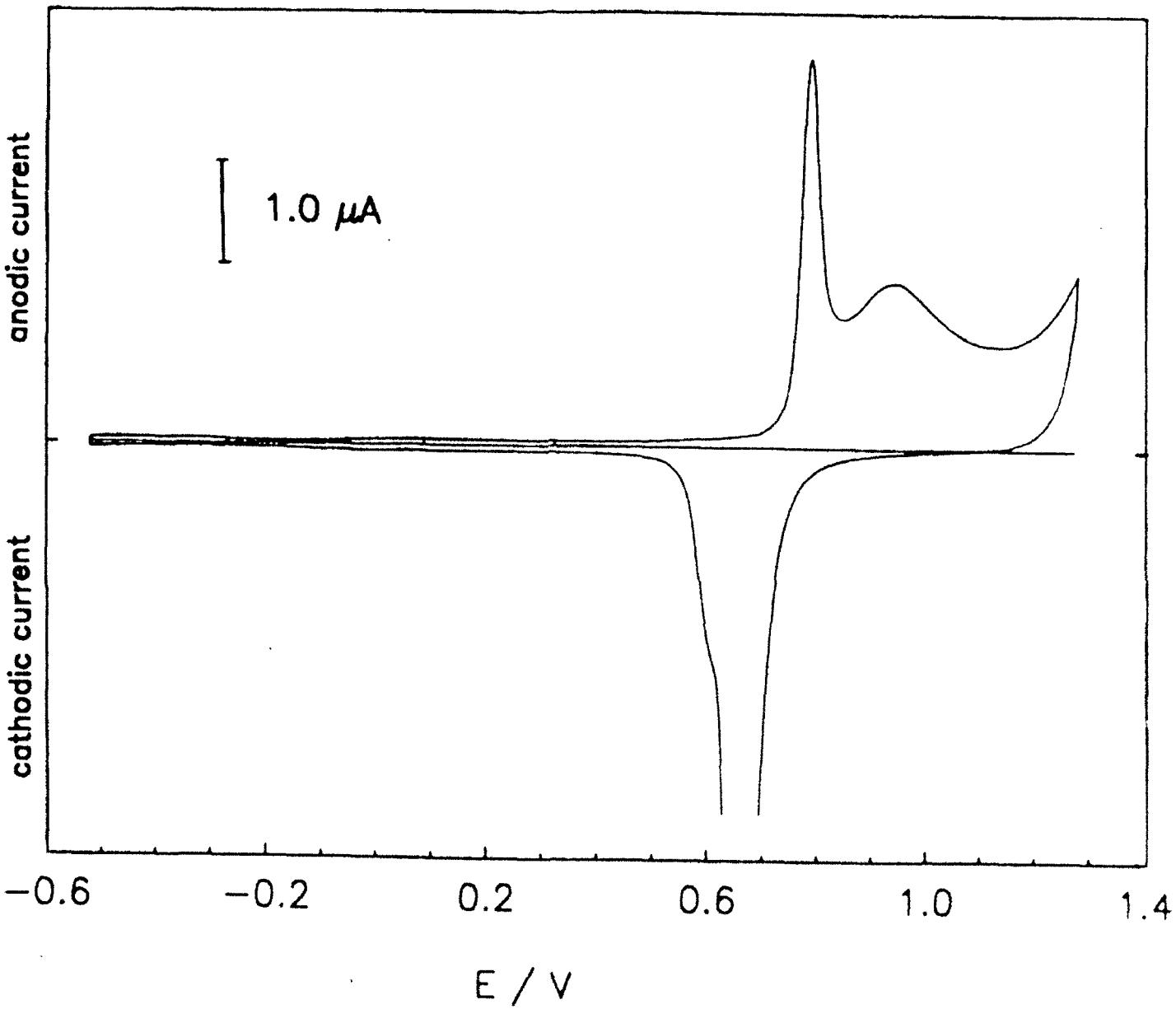

Figure 1.a

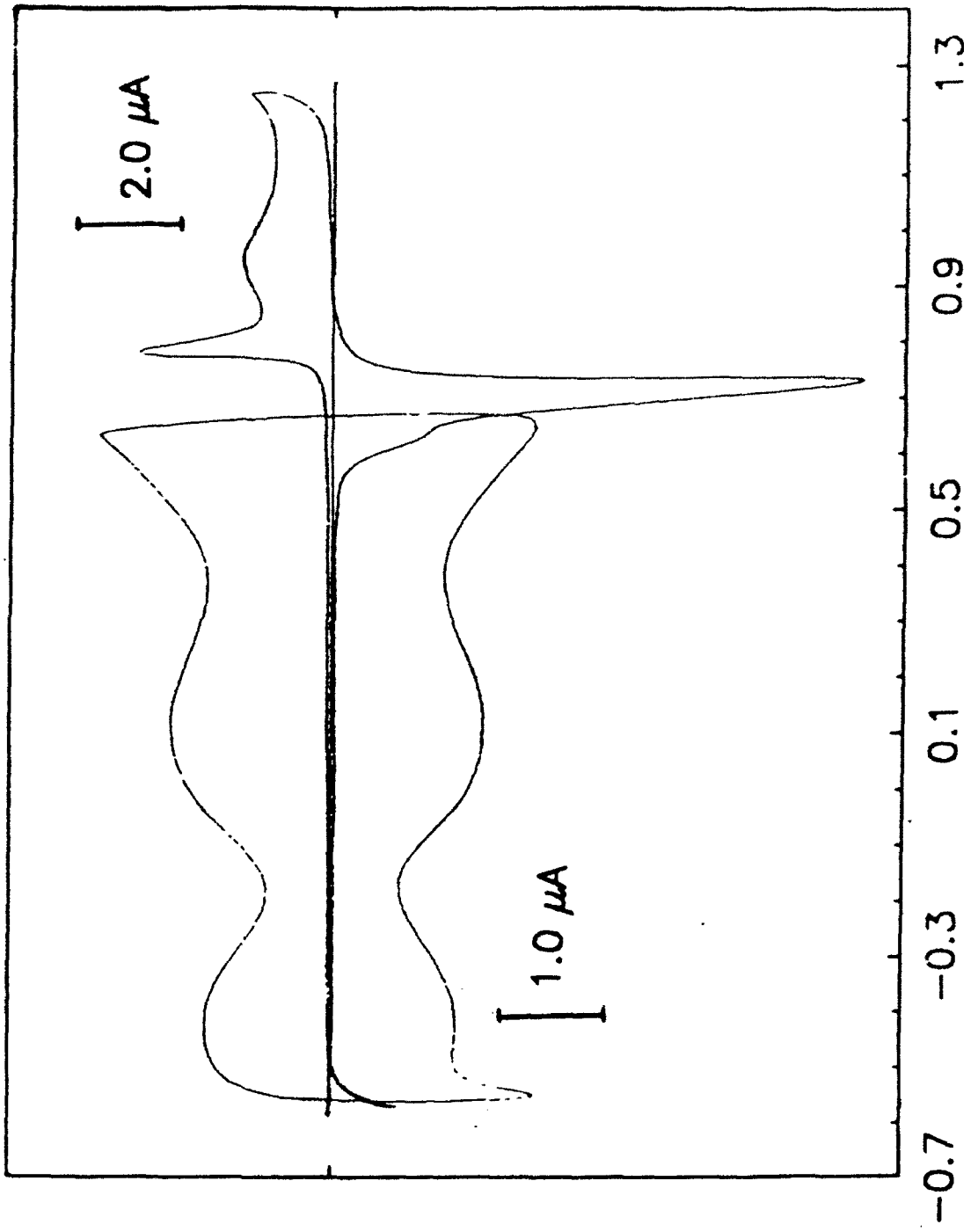

Figure 1.b

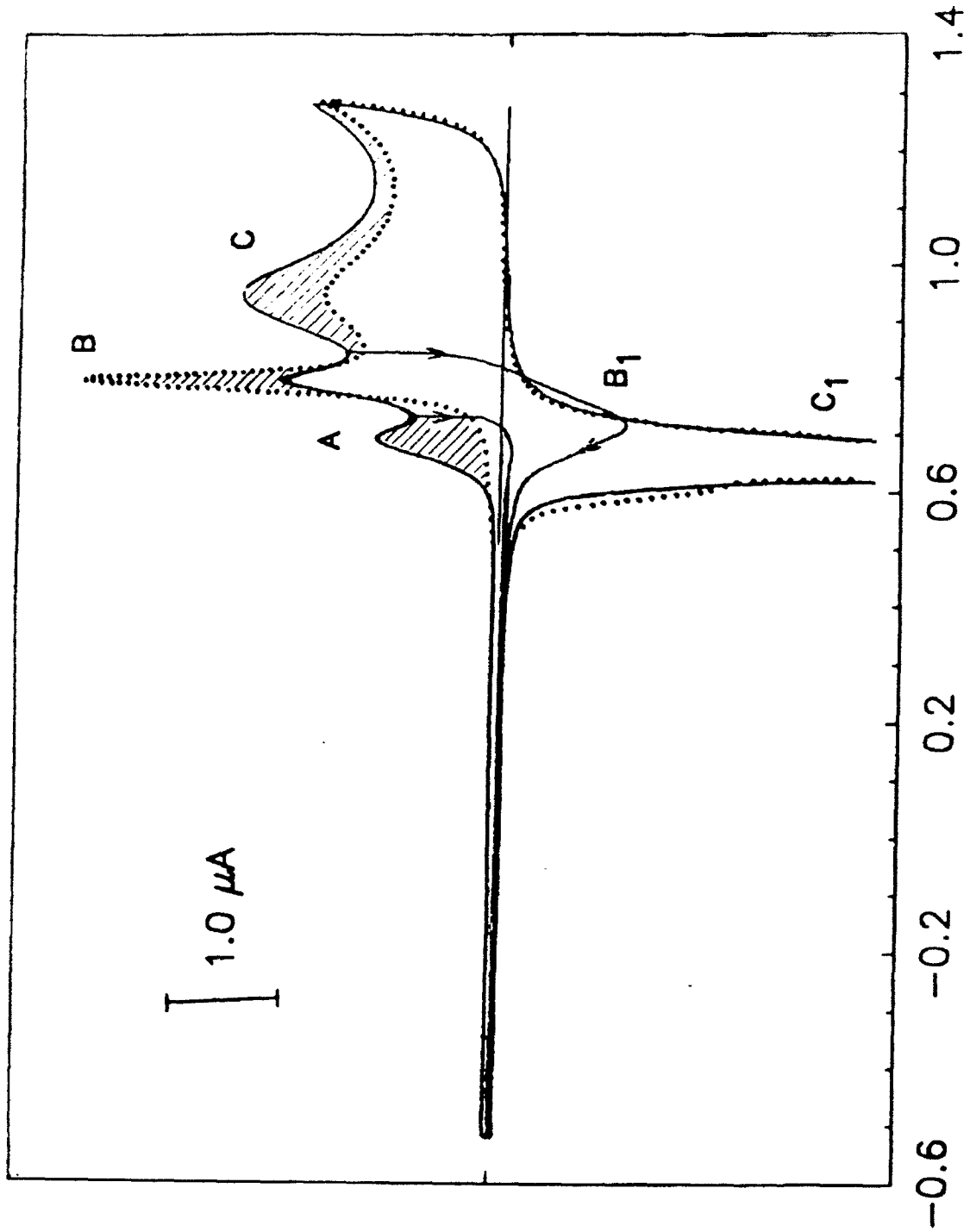

Figure 2.

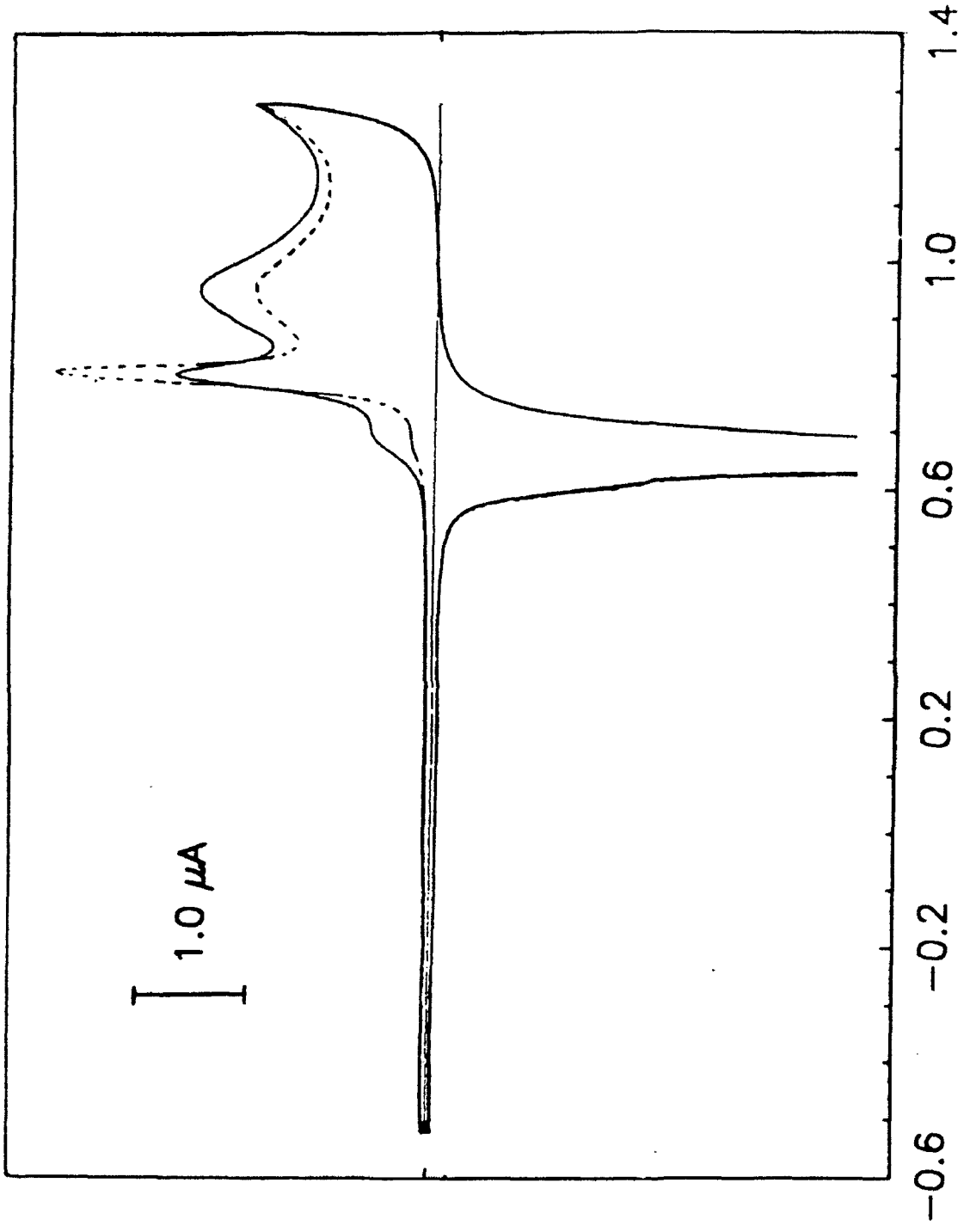

Figure 3.a

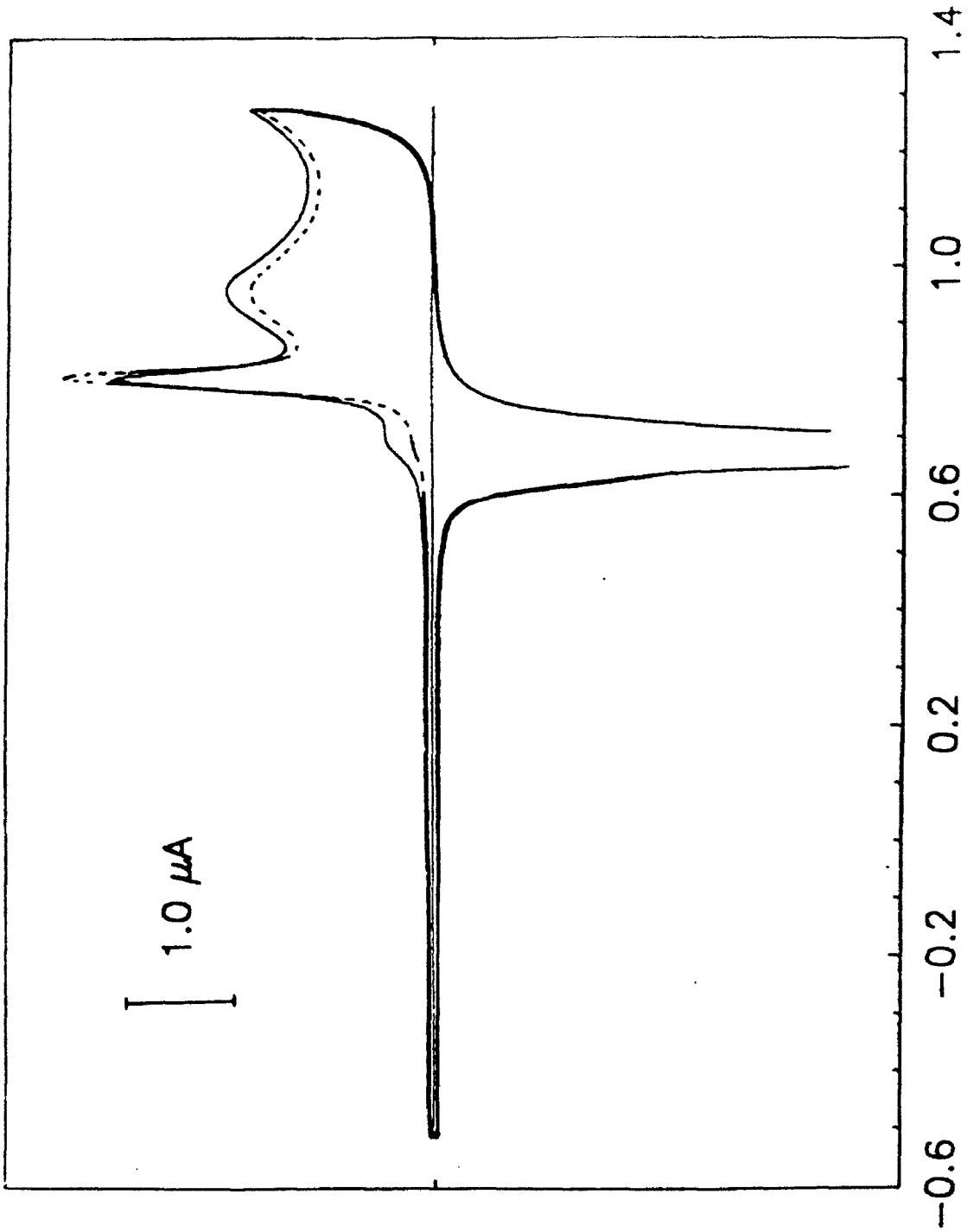

Figure 3.b

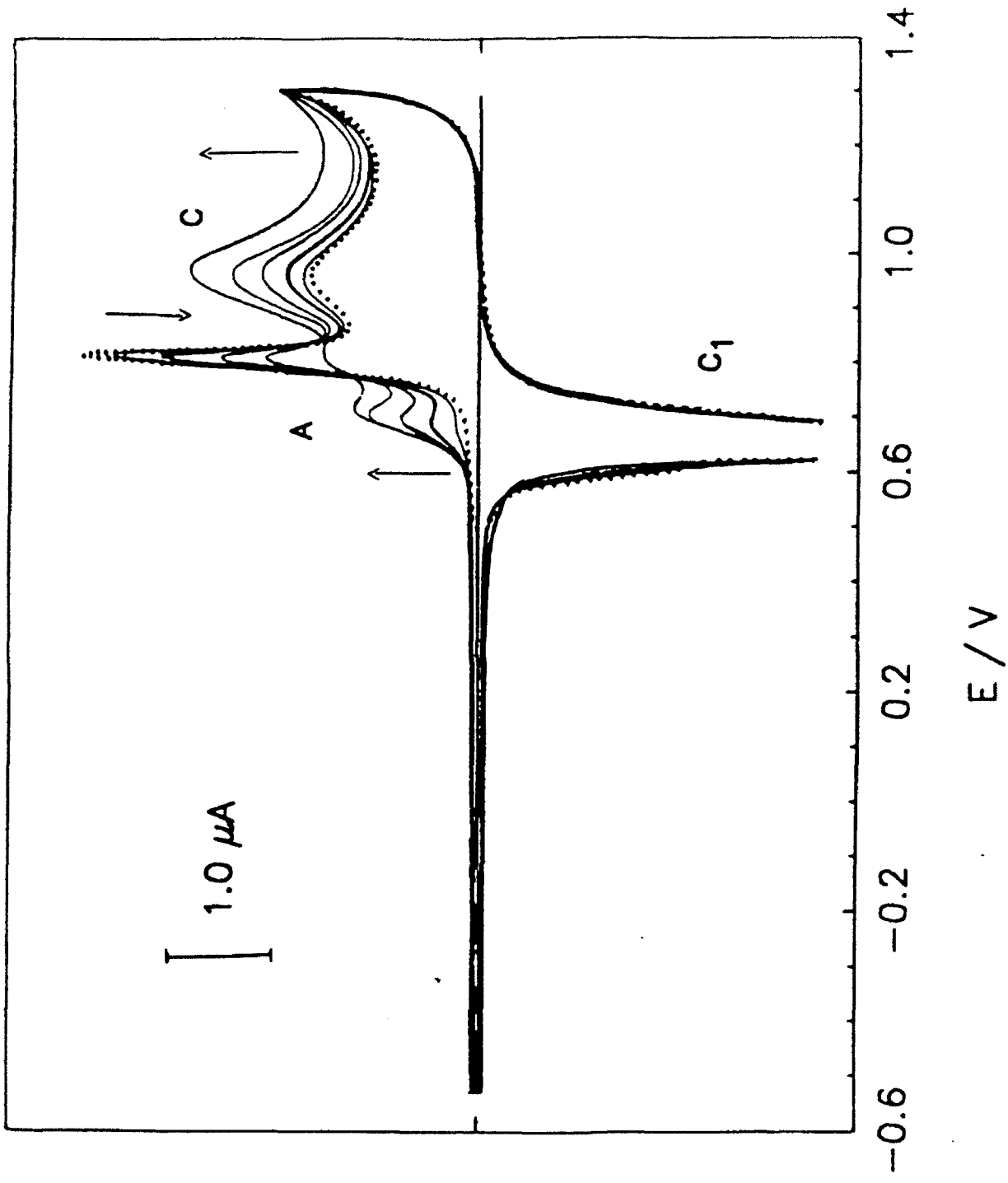

Figure 4.a

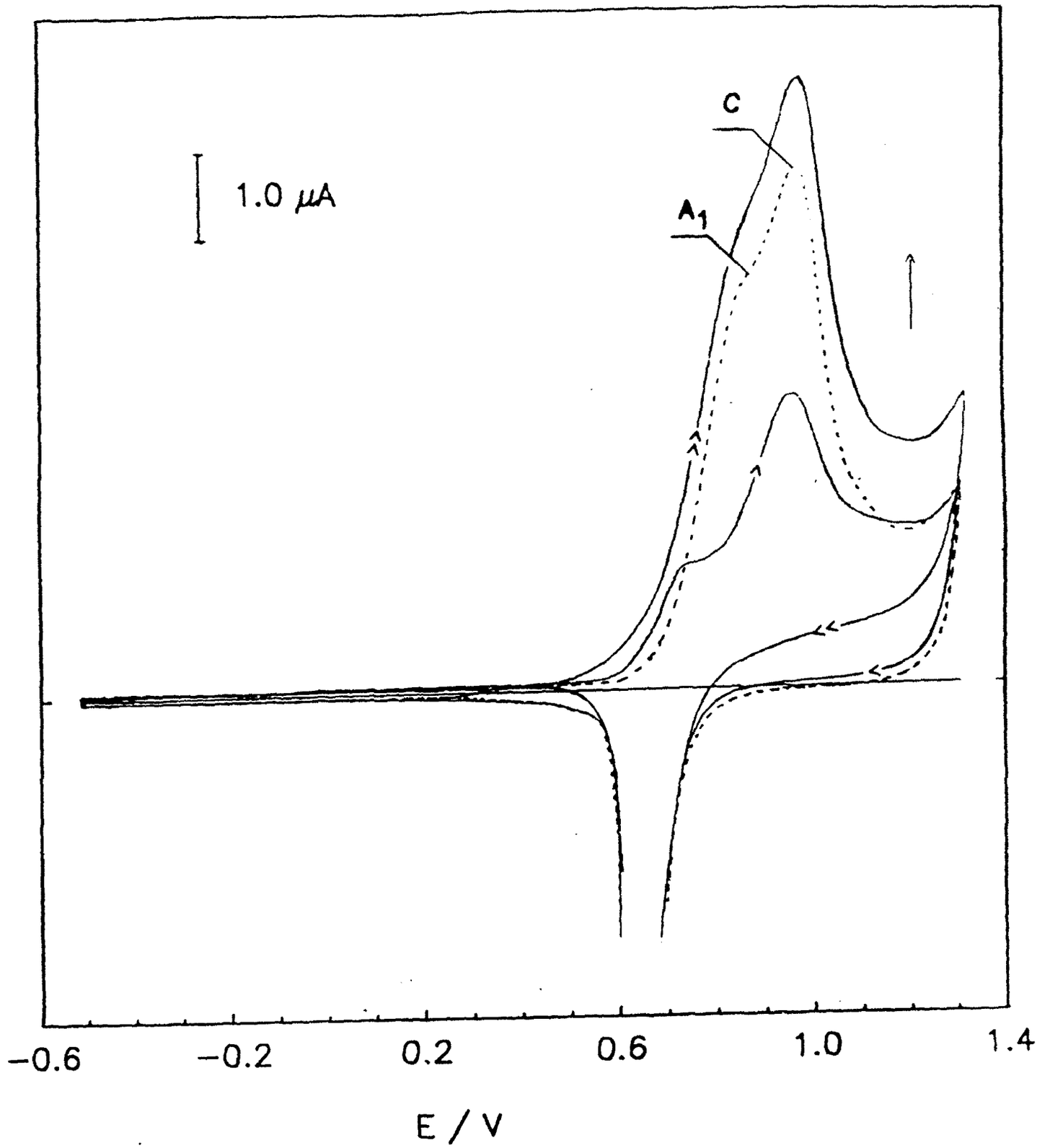

Figure 4.b

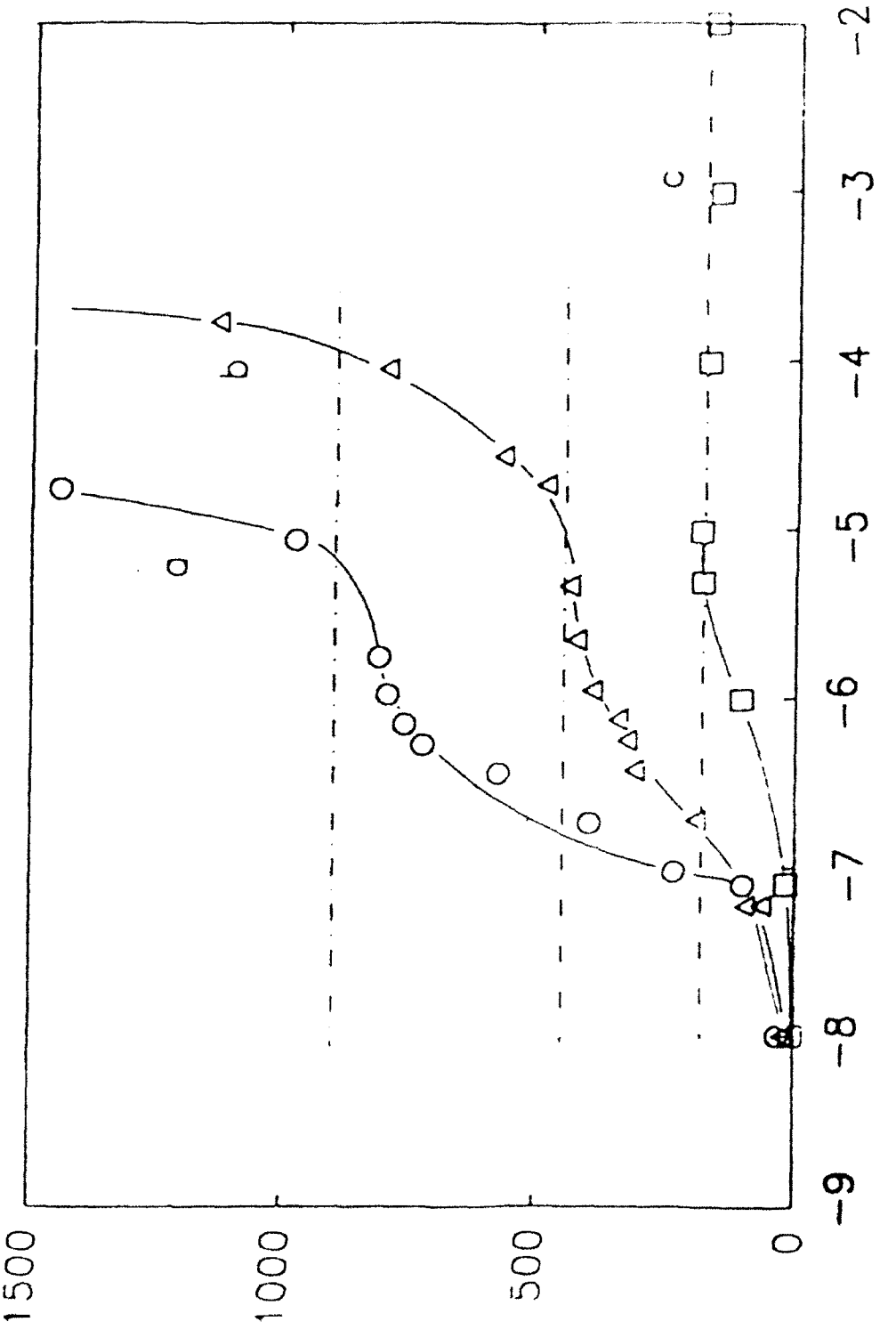

Figure 5

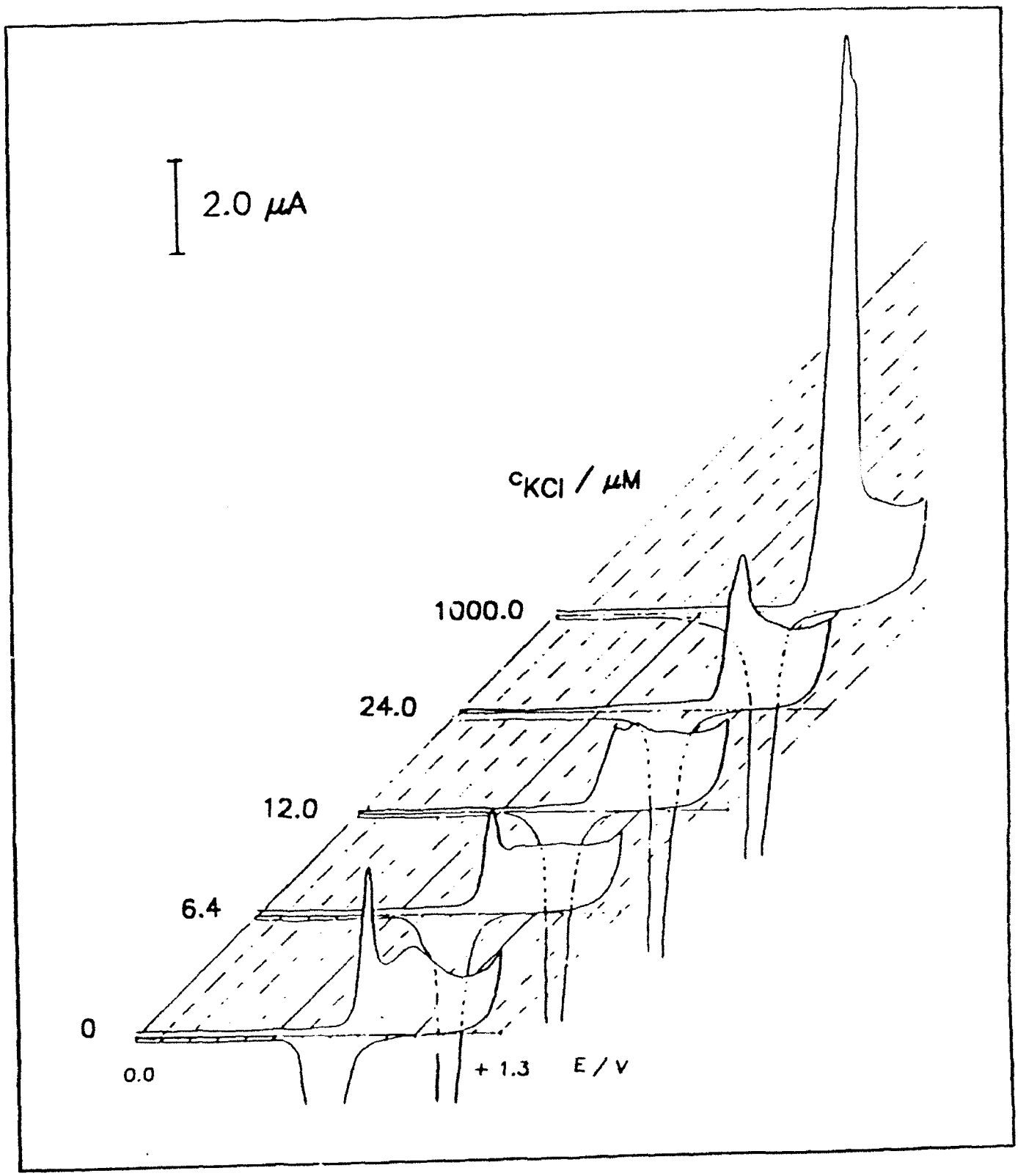

Figure 6.a

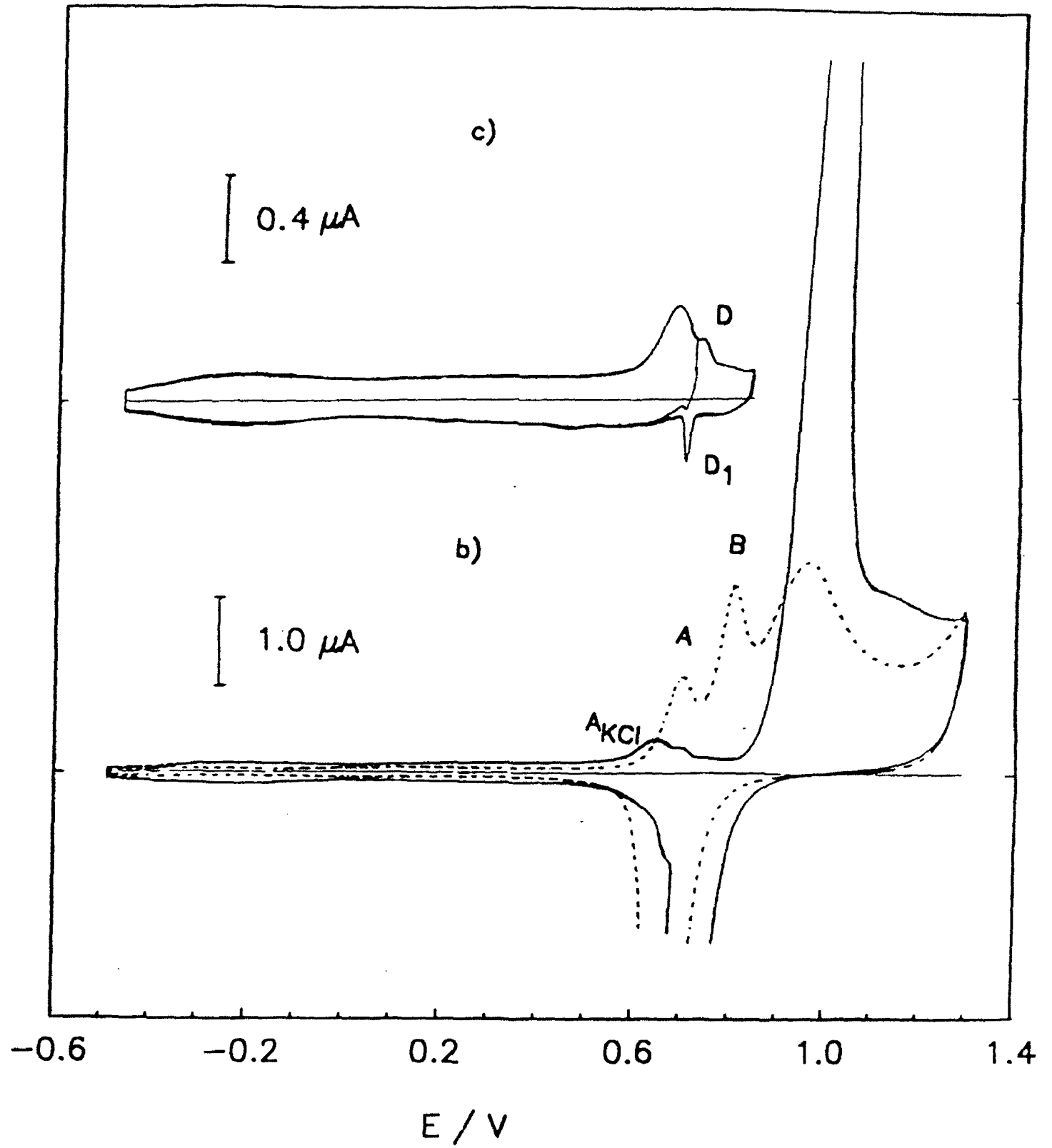

Figure 6.b and 6.c

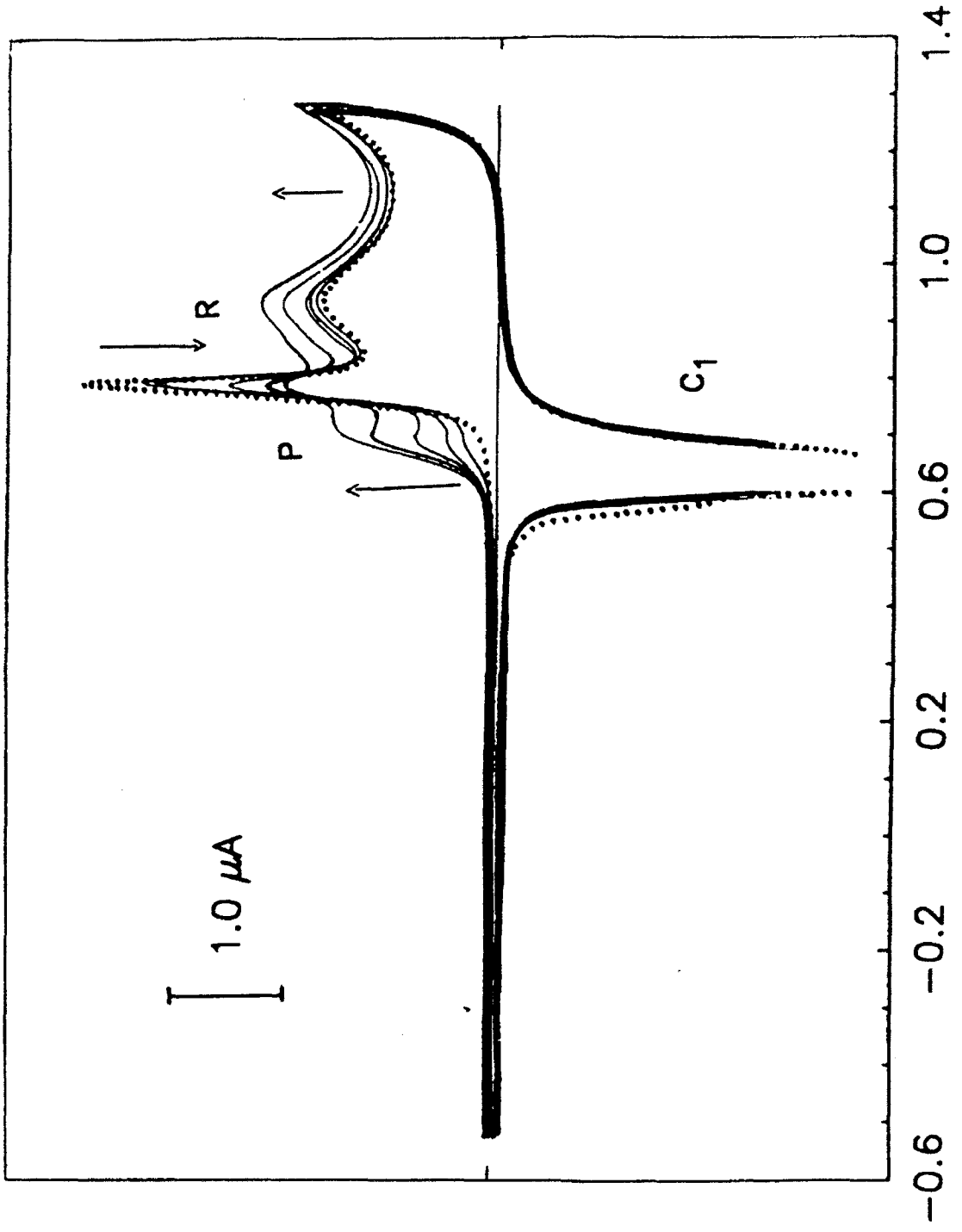

Figure 7.a

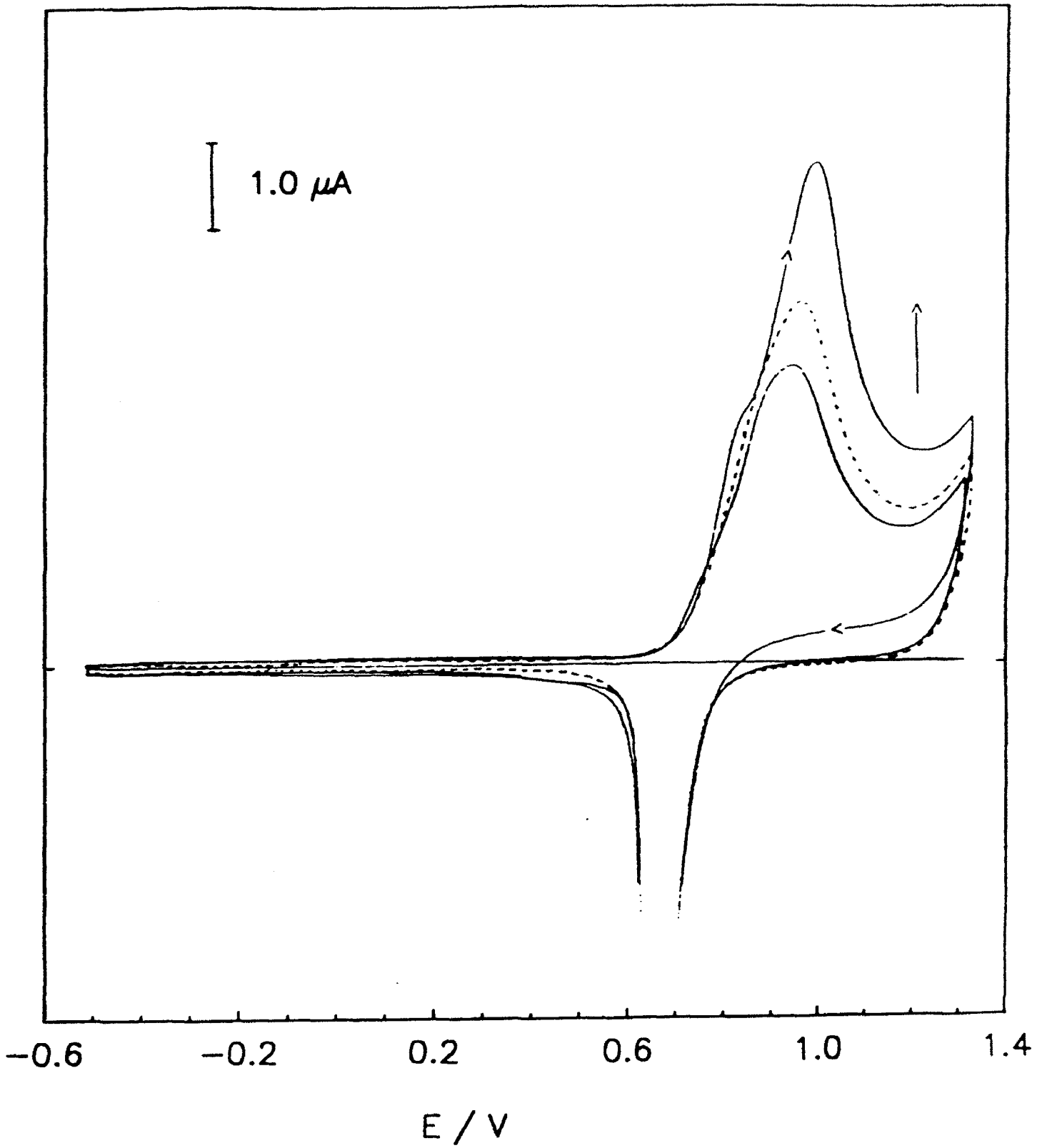

Figure 7.b

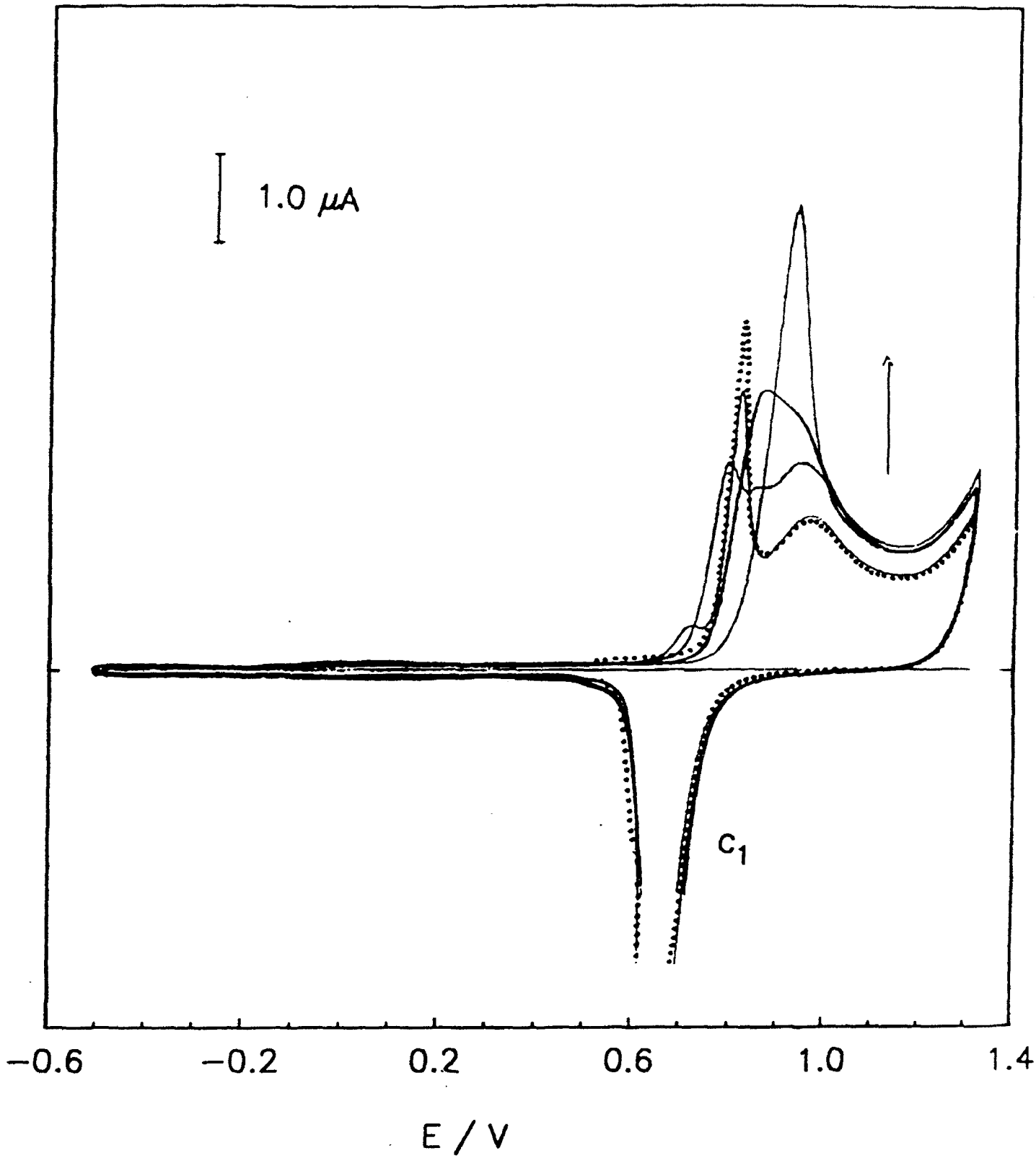

Figure 8